

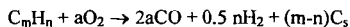
THE CARBON MONOXIDE-ELEMENTAL CARBON LINK:
A METHODOLOGY FOR DIAGNOSING AND MONITORING SOOT IN URBAN AREAS

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BACKGROUND

Carbon monoxide (CO) and elemental carbon (soot) are produced in large quantities by incomplete combustion in urban areas. The effects of soot on health (*Dockery et al.*, 1992, 1993), photochemical processes (*Raga and Raga*, 1999) and on structural damage (*Mansfield et al.*, 1991; *Pio et al.*, 1998) has raised the scientific and public consciousness of the need to better understand and monitor soot formation, evolution, and transport, as well as its catalytic potential for surface heterogeneous reactions. The measurement and monitoring of CO is common in the large urban areas of first world countries and becoming more frequent in the cities of developing countries. The measurement of soot mass is more problematic because of its particulate nature and difficulty in quantification; however, because of its ubiquitous nature and potential for environmental damage at so many different levels, there is a serious need to assess its magnitude, both spatially and temporally. Recent measurements in Mexico City show a high correlation between CO and the light absorption coefficient, σ_a , and optical property of aerosols that is linearly related to the mass mixing ratio of soot (*Fuller et al.*, 1999). As a result, there is a possibility that CO can be used as a surrogate for soot concentrations if the physical basis for the link between these two atmospheric components is well understood.

There is a obvious link between CO and soot since both are produced in abundance during inefficient combustion processes. The formation of soot depends on the carbon/oxygen ratio in the hydrogen-air mixture during combustion. The combustion stoichiometry is (*Seinfeld and Pandis*, 1998)



where C_s is the soot formed and the ratio of carbon to oxygen is $m/2a$. The C/O ratio is critical for determining the amount of soot formed, i.e. if there is sufficient oxygen to tie up all available carbon as CO, then no soot will form. With less and less oxygen, more soot is formed. Thus, one would expect the relationship between CO and σ_a to be related to altitude, fuel composition, and combustion efficiency.

In the following sections, the measurement techniques and sampling site will be discussed, followed by an analysis of five, continuously high pollution days that represent typical conditions in a urban area. The presentation is closed with some preliminary conclusions and recommendations for additional studies.

MEASUREMENT AND ANALYSIS METHODOLOGY

The experimental site was located within the Mexico City Ajusco Ecological Reserve (19° 15' N, 99° 11' W), in the southwest corner of the Mexico City basin, at an elevation 440 m above the average city level of 2240m. This site provided measurements in the residue of the city's mixed layer at night and early morning, and in the polluted mixed layer that enveloped the site during the day. The field campaign extended from 4 to 18 November 1997, a period that is normally near the end of this region's rainy season.

Continuous measurements at a sampling rate of 1 Hz were made of carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen oxides (NO, NO_x) and ozone (O₃). The total scatter and hemispheric back scatter coefficient of aerosols were measured at three wavelengths (450, 550, 700 nm) with a nephelometer and the absorption coefficient, σ_a , with a particle soot absorption photometer (PSAP, Radiance Research Corp.), after the particles were first passed through a 1 µm cut-size impactor and heated to insure a relative humidity less than 40%. The PSAP measurements were corrected for light scattering and other effects that bias the absorption measurements using the suggested factors of *Bond et al.* (1999). The optical coefficients were averaged at one minute intervals, and taken 24 hours a day. Visible and ultraviolet solar radiation

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were measured with hemispheric radiometers. Meteorological measurements (wind speed and direction, temperature and relative humidity) were also recorded. The equipment was installed in a building within the Reserve, with all gas and aerosol samples taken from air coming through a chimney that extended above the building by approximately two meters (a total of approximately 8m above the ground) and ventilated with a flowrate of approximately 90 l min^{-1} . The meteorological measurements were made at the same elevation as the top of the stack, about three meters to the north. All the measurements were processed into six minute averages that corresponded to the accumulation interval of the DMA.

The remainder of this paper focuses on the measurements made of CO , σ_a , and wind.

RESULTS AND DISCUSSION

Five days during the research period were selected for the evaluation of the $\text{CO} - \sigma_a$ relationship, November 14-18, 1997. These days were selected since they are days with high ozone levels representative of the typical high pollution days in Mexico City. Figure 1 illustrates the daily trends in CO , O_3 , and σ_a over this five day period.

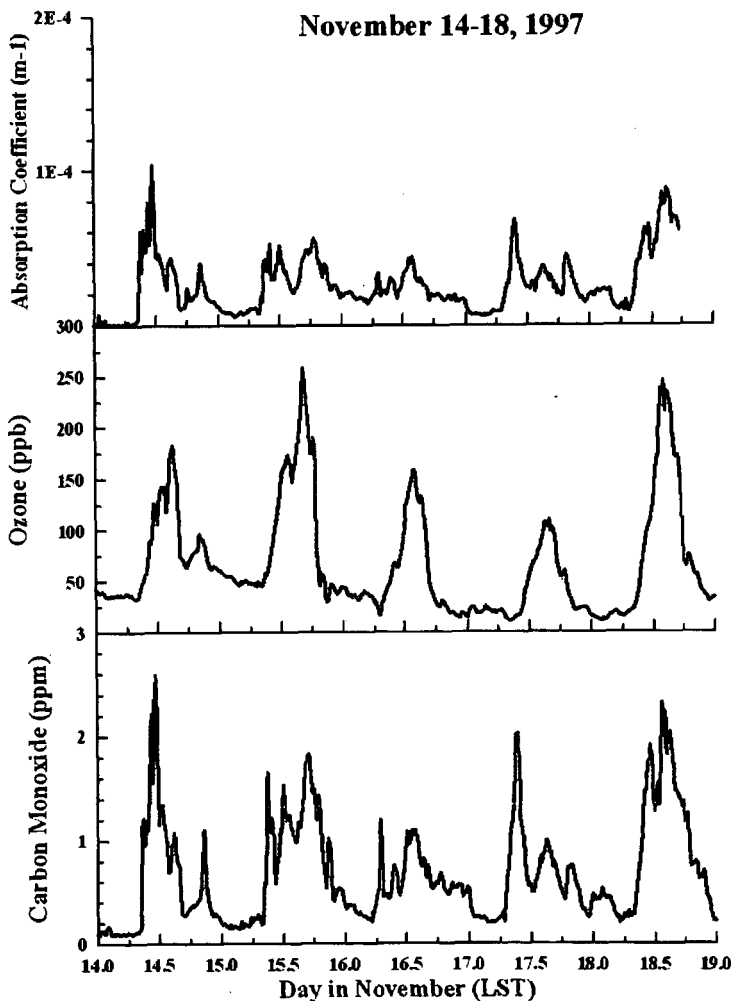


Figure 1

The initial rapid increase in CO occurs as the morning airflow shifts to a southwesterly direction and emissions from early morning traffic are transported up the hillside to the research site. As the sun rises and heats the Mexico City basin, the atmospheric mixed layer develops and grows to an altitude higher than the measurement site. Ozone increases with increasing actinic fluxes during the day. The relationship between CO and σ_a is clearly seen in Fig. 2 as the trends for one of the days, November 14, are displayed for the time period between 6:00 and 18:00 LST.

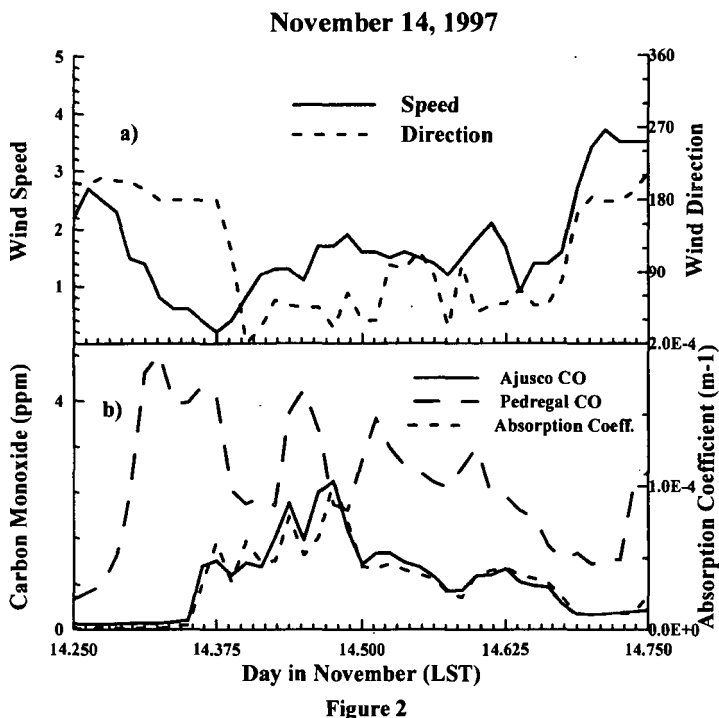


Figure 2b clearly shows that the σ_a changes with CO at the research site. Also presented in this figure is the CO measured upwind, in the city basin at one of the city's pollution monitoring sites (Pedregal). This particular research site is approximately two kilometers to the north of the Ajusco. When the winds are southerly at average speeds of 2 ms^{-1} (Fig. 2a), the CO measured at the Ajusco site represents the city level CO that has aged approximately one and a half hours. The CO normally decreased by about 50% from the city to the research site. This decrease occurred mostly as a result of dilution.

Figures 3 and 4 are scatter diagrams of σ_a Vs CO for all five days (Fig. 3) and four the 14, 16, and 17 of November only. The linear regression of σ_a as a function of CO, and Pearson correlation coefficient were computed and are shown on the two figures. These figures indicate a very good linear correspondence between σ_a and CO, reflected in statistically significant correlation coefficients, i.e. an indication that a first order polynomial fits the data well with high confidence levels. There is a certain degree of scatter, however, a group of points that appears to have a similar slope as the best fit line, but with an offset that could either be a decrease in σ_a or increase in CO. These data originate primarily from November 15 and 18, as seen in Fig. 4, where these days have been removed from the analysis. The slope and offset of the best-fit line, excluding these two days, is not significantly different and the correlation coefficient increases only slightly.

Further analysis of the relationship between σ_a and CO, with respect to meteorological conditions and other anthropogenic emissions, e.g. O_3 and NO_y , indicate that the linear regression coefficients of σ_a Vs CO remain remarkably constant regardless of local meteorology or other emission indicators.

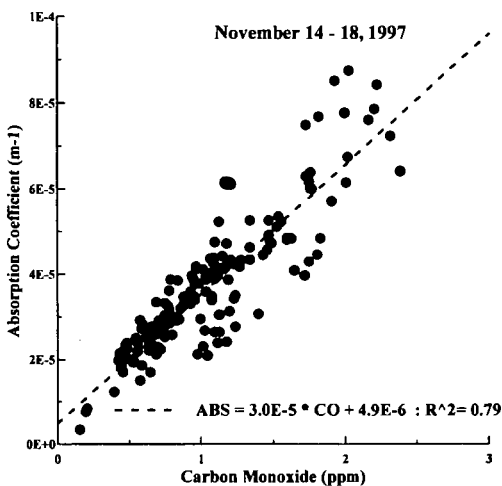


Figure 3

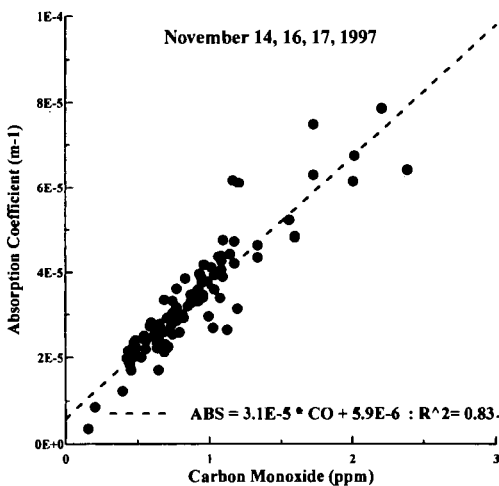


Figure 4

The positive offset, indicated by the non-zero intercept of the best-fit line, suggests that there is possibly some type of hysteresis that occurs on a daily basis, i.e. that there is a residual of soot aerosols that remain aloft when the mixed layer decays in the afternoon. When the five days were analyzed on an individual basis, although the slopes of the best-fit lines remained approximately 3×10^{-5} , the offsets ranged from $1 - 12 \times 10^{-6}$. This might be related to the previous days soot levels and maximum height of the mixed layer; however, additional evaluation of the measurements are needed before this can be better ascertained.

SUMMARY

As the amount of soot and CO produced by combustion is proportional to the type of fuel that is used and the amount of available oxygen, it is likely that the soot-CO relationship can vary from city to city. In addition, the current measurements were made several kilometers distant and 1-2 hours of aging downwind of the primary sources. Since the mixing and dilution processes are different for gases and aerosols, the CO- σ_a relationship may possibly depend upon the distance from emission sources, as well.

The ability to estimate soot from CO measurements is highly promising, however, because of the ease of measuring CO compared to soot, the abundance of past CO measurements that could be analyzed with this relationship, and the potential for better monitoring of soot in the future. Evaluation of this relationship continues at UNAM with a current focus on measuring CO and σ_a closer to emission sources in the city. The evaluation will concentrate on further refining the CO Vs σ_a relationship and understanding how other factors potentially affect this relationship.

The absorption coefficient is a useful parameter for assessing decreases in optical depth and the subsequent effect on radiative fluxes and impacts on photochemistry and climate change. The soot mass, however, is very important when evaluating the impact on health and heterogeneous processes. Hence, filter samples of aerosols are being analyzed to measure the soot mixing ratio. These will be used to estimate the specific absorption of Mexico City soot in order to convert absorption measurements to mixing ratios.

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REFERENCES

- Fuller, K.A., W.C. Malm, and S.M. Kreidenweiss, 1999: Effects of mixing on extinction by carbonaceous particles, *J. Geophys. Res.*, 104, 15,941 - 15,954.
- Bond, T.C., T.L. Anderson, and D. Cambell, Calibration and intercomparison of filter-based measurements of visible light absorption by aerosols, *Aerosol Sci. and Tech.*, 30, 582-600, 1999.
- Dockery, D.W., J. Schwarz, and J.D. Spengler, Air pollution and daily mortality; associations with particulates and acid aerosols, *Environ. Res.*, 59, 362-373, 1992.
- Dockery, D., W. C.A. Pope, X. Xu, J.D. Spengler, J.H. Ware, M.E. Fay, B.G. Ferris Jr., and F.E. Speizer, An association between air pollution and mortality in six U.S. cities, *New England J. Med.*, 329, 1753-1759, 1993.
- Mansfield, T.A., R. Hamilton, B. Ellis and P. Newby, 1991: Diesel particulate emissions and the implications for the soiling of buildings, *Environmentalist*, 11, 243-254.
- Pio, C.A., M.M. Raamos, and A.C. Duarte, 1998: Atmospheric aerosol and soiling of external surfaces in an urban environment, *Atmos. Env.*, 32, 1979 - 1989.
- Raga, G.B. and A.C. Raga, On the formation of an elevated ozone peak in Mexico City, *Atmos. Env.*, Submitted, 1999.
- Seinfeld, J.H. and S.N. Pandis, 1998: Atmospheric chemistry and physics, John Wiley and Sons, N.Y., 1326 pp.